Coexistence of Superconductivity and Ferromagnetism in Dilute Co-doped $La_{1.89}Ce_{0.11}CuO_{4\pm\delta}$ System

K. Jin, J. Yuan, L. Zhao, H. Wu, X.Y. Qi, B.Y. Zhu, L.X. Cao, X.G. Qiu, B. Xu, X.F. Duan, and B.R. Zhao*
National Laboratory for Superconductivity, Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, P. O. Box 603, Beijing 100080, China
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Thin films of the optimally electron-doped T'-phase superconductor $La_{1.89}Ce_{0.11}CuO_{4\pm\delta}$ are investigated by dilute Co doping, formed as $La_{1.89}Ce_{0.11}(Cu_{1-x}Co_x)O_{4\pm\delta}$ (LCCCO) with $x = 0.01$ – 0.05. The following results are obtained for the first time: for the whole dilute Co doping range, LCCCO thin films show long-range ferromagnetic ordering at the temperature range from 5 K to 300 K, which is likely due to the RKKY interaction; in the very dilute Co doping, $x = 0.01$ and 0.02, the superconductivity is maitained, the system shows the coexistence of superconductivity and ferromagnetism in the CuO_2 plane. This may be based on the nature of the charge carriers in electron-doped high-T_c cuprate superconductors.

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An important progress in superconductor physics is the observation of coexistence of superconductivity (SC) and ferromagnetism (FM) in the spin-triplet pairing superconductors, such as UGe_2,[1] $ZrZn_2$[2] and URhGe.[3] For high-T_c cuprate superconductors (HTSC), it is commonly believed that the CuO_2 plane plays an important role in SC. Therefore, seeking for the possibility of coexistence of SC and FM in the CuO_2 plane is very helpful for us to understand the interaction between SC and magnetism, and the mechanism of SC. The $RuSr_2GdCu_2O_8$ (Ru-1212) is well known for the feature of coexistence of SC and FM, but the study shows that the SC takes place in the CuO_2 plane while the FM forms in the RuO_2 plane.[4] In the past years, the effect of magnetic impurity doping in the CuO_2 plane has been an important issue for HTSC. Many works have been done on the substitution of a magnetic Ni-ion (Fe, Co, etc. are also included in some works) for a Cu-ion in $(La,Sr)_2CuO_4$, $YBa_2Cu_3O_7$, $Bi_2Sr_2CaCu_2O_8$, and their related ones.[5] For comparison, the same works have been done on the nonmagnetic Zn-ion substitution.[6] The study of the impurity doping effect has provided a great deal of information about the nature of the cuprates. However, there have been no reports on the possible coexistence of SC and FM in the CuO_2 plane.

It should be particularly pointed out that most of the previous experiments on the magnetic impurity doping effect are focused on the hole-doped HTSC, and only a few works have been addressed on the electron-doped ones.[7] This mainly attributed to the relatively lower T_c ($\leq$ 30 K) and more complicated preparation process of the electron-doped HTSC. However, the electron-doped HTSC have their own intriguing properties, especially the two-band model and two types of charge carriers (electrons and holes) are confirmed experimentally and theoretically.[8,9,10] It will be interesting and challenging for us to deeply explore the interaction of SC and FM related the CuO_2 plane by magnetic impurity doping in the electron-doped HTSC, since even for the case of Ru-1212, the two-band model and two kinds of charge carriers are considered to be the origin of the coexistence of SC and FM.[11]

In the present work, thin films of the optimally electron-doped T'-phase superconductor $La_{1.89}Ce_{0.11}CuO_{4\pm\delta}$ (LCCO) are investigated by dilute Co doping at the Cu site. Through the systematic transport and magnetization measurements of $La_{1.89}Ce_{0.11}(Cu_{1-x}Co_x)O_{4\pm\delta}$ (LCCCO) thin films with $x = 0.01$ – 0.05, together with reduction treatment and valence examinations, some interesting new effects are found contrasting to the previous works: the long-range FM ordering is observed in the temperature range of 5 K – 300 K for all the designed Co doping concentrations, $x = 0.01$ to 0.05, which is suggested to be formed by the RKKY interaction; for the cases of very dilute Co concentrations, $x = 0.01$ and 0.02, the coexistence of SC and FM at the temperatures below T_c in the CuO_2 plane is obviously detected; the electrons play an important role for SC in LCCO system.

The optimally doped LCCO is used as the benchmark material for the present Co doping study, since its normal state is in a completely metallic phase and it has the highest T_c ($\sim$ 30 K) in the electron-doped HTSC family,[12] we can easily test the influence of Co substitution for Cu[13] on SC at relatively high temperatures. The condition of preparation of LCCCO thin films is similar to the case of LCCO ones as described in detail elsewhere.[14,15] The stoichiometric targets with the atomic ratio of La:Ce:Cu:Co = 1.89:0.11:(1-x):x were fabricated by a solid state reaction process. Then LCCCO thin films with $x = 0.01$, 0.02, 0.04 and 0.05 were deposited on (001)-oriented $SrTiO_3$ (STO) substrates by dc magnetron sputtering with $\sim 250\ nm$ thickness each. X-ray diffraction (XRD) data show that all the thin films are in single T'-phase and (001)-oriented. Fig. 1 shows the [010] zone axis high resolution electron microscopy (HREM) image and the corresponding electron diffraction pattern of the film with $x = 0.05$, which indicates

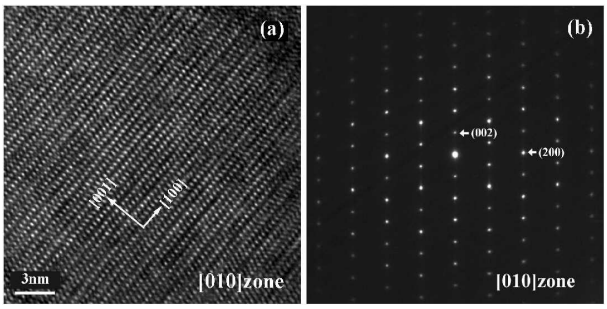

FIG. 1: The [010] zone axis HREM image (a) and its corresponding electron diffraction pattern (b) of LCCCO sample with Co concentration $x = 0.05$.

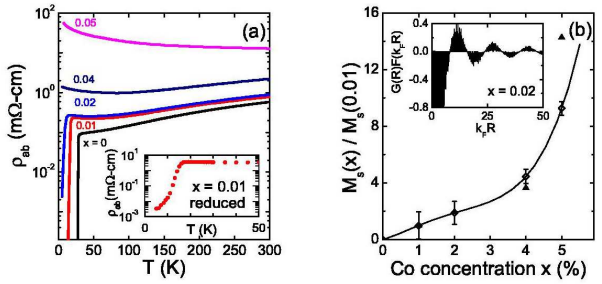

FIG. 2: (Color online) (a) In-plane resistivity ρ_{ab} versus temperature for the films with Co concentration $x = 0$, 0.01, 0.02, 0.04, 0.05. Inset: $\rho_{ab}(T)$ of the reduction-treated film (after 3 times annealing) with $x = 0.01$. (b) $M_S(x)$ obtained by 2D damped RKKY model characterization (normalized by $M_S(x = 0.01)$ with $l = 50$ Å, $k_F = 0.8$ Å^{-1}. Triangles and diamonds represent experimental data and calculated value, respectively. Solid line is the fit for the data. The error bars are from the statistical errors for 100 times calculations. Inset: typical oscillating behavior of $G(R)F(k_FR)$ versus k_FR for the thin film with $x = 0.02$.

a perfect structure. In order to examine the electric and magnetic properties, the in-plane resistivity and magnetization were measured. All measurements were carried out using a Quantum Design MPMS-5 equipment. In order to measure the resistivity, the samples were patterned into the bridges with width of 50 μm. Then the Ag electrodes were deposited on the surfaces of the films through a metal mask. The in-plane resistivity $\rho_{ab}(T)$ data as shown in Fig. 2 (a) indicate that the samples with $x = 0.01$, 0.02 are superconducting, with zero resistance temperature $T_{c0} \sim 13$ K and < 5 K, respectively. T_{c0} is ~ 27 K for the pure LCCO thin film (with $x = 0$). While the samples with $x = 0.04$ and 0.05 tend to be insulator-like with decreasing T down to 5 K. The magnetization versus temperature $M(T)$ curves, with magnetic field $H = 1000$ Oe (parallel to the CuO_2 plane), show the evolution from superconductor to ferromagnet with increasing Co concentration. The magnetization $M(H)$ measurements are also done for all the designed Co-doped thin films, and the clear hysteresis loops indicate that a real FM long-range ordering rather than other magnetic phase[16] forms even for the very dilute Co concentration, $x = 0.01$. With increasing Co concentration, the FM ordering enhances. It can be clearly observed in Fig. 2 (b) that the saturation magnetization M_S for the film with $x = 0.05$ is more than 10 times larger than that of the film with $x = 0.01$.

Surprisingly, $M(H)$ data for the samples with $x = 0.01$ and 0.02 definitely show the coexistence of SC and FM in the superconducting transition region. In Fig. 3, four typical $M(H)$ curves are presented: (a) a superconducting $M(H)$ curve for the sample with $x = 0.01$ is observed at the temperature (T = 5 K) lower than T_{c0}; (b) the full ferromagnetic hysteresis loop for the same sample at 30 K (higher than T_c); (c) the $M(H)$ data of the sample with $x = 0.02$ give clearly evidence for the shielding effect in low field region (indicated by OM, with H_{c1} of ~ 50 Oe at 5 K). However, with increasing H, SC is suppressed and FM becomes dominant in the sample; (d) with increasing the temperature up to 25 K (higher than T_{c0}), the curve for the same sample with $x = 0.02$ is transformed into a full FM hysteresis loop. These four loops obviously reveal the coexistence and competition of SC and FM in the very dilute Co concentrations.

For the origin of FM ordering in LCCCO, several possibilities should be considered.[17] One is the segregated Co clusters that can be formed if the Co atoms can not dissolve into the lattice of the LCCO. If such dilute Co atoms gather to form FM, the large area of the film must be Co-ion-free, which results in seperation of SC basis with a few FM clusters, and then no above regular influence of Co doping on SC can be observed. Furthermore, We grew (103)-oriented LCCCO thin films on the miscut (110)-oriented STO substrates in the same batch with the (001)-oriented sample. The process is similar to the growth of (103)-oriented LCCO thin films.[14] The magnetization data show that the M_S in (103) plane is $\sim 1.4 \times 10^{-5}$ emu, obviously smaller than the $M_S \sim 1.8 \times 10^{-5}$ emu in (001) plane. Such anisotropy of M_S strongly suggestes that the FM ordering should not originate from the segregated Co clusters. Actually, no Co cluster is observed in other Co-doped systems, such as the Co-doped SnO_2[18] and ZnO,[17] in which the long-range FM ordering with the Curie temperature higher than room temperature is formed, while no Co cluster is observed. Another possible origin of the FM ordering, i.e., the Co oxides, can also be excluded, because almost all of the Co oxides are antiferromagetic or ferrimagnetic.

Therefore, the Ruderman-Kittle-Kasuya-Yosida (RKKY) interaction, i.e., the coupling of the localized magnetic moments via polarized charge carriers, should be the dominant mechanism for the FM ordering in the present LCCCO system. Here, a 2D damped RKKY interaction model[19] is used to characterize the experimental data. The RKKY interaction can be given

as the form,[19,20]

$$H = \frac{J^2V^2m^*k_F^2}{8\pi^2\hbar^2N^2}\sum_{\substack{ij\\ i\neq j}}\exp(-\frac{R_{ij}}{l})F(k_FR_{ij})\boldsymbol{S}_i\cdot\boldsymbol{S}_j, \quad (1)$$

with $$F(x) \equiv J_0(x)N_0(x) + J_1(x)N_1(x),$$

where J, m^*, k_F, S_i, and R_{ij} are respectively the interaction between the local magnetic moment and the polarized carrier, the effective mass of the conduction carrier, the Fermi wave vector, the ith Co local moment, and the distance between S_i and S_j moments; V and N denote the volume and the cell numbers of the samples, respectively; l is the mean free path of the carriers; J_i and N_i ($i = 0,\ 1$) are the first and the second Bessel functions, respectively. Employing a simplified Monte Carlo method,[17] we can rewrite Eq. (1) as $H_{RKKY} = C(S\cdot S)\sum_R \exp(-R/l)G(R)F(k_FR)$, with constant C and S (spin), the Co-ion distribution function $G(R)$, and the oscillating function $F(k_FR)$. If the sum of Eq. (1) is negative, the FM can be achieved favorably. For each Co doping case, we make calculations in a 2D 2500 × 2500 lattice and average in 100 times. Since this sum is not sensitive to k_F so long as assuring it is negative (FM forms), it is reasonable to choose $k_F = 0.8$ Å^{-1}. We set $l = 50$ Å in order to keep the carriers moving well. Then the reduced M_s for each Co concentration is obtained from the sum of $\exp(-R/l)G(R)F(k_FR)$,[20,21] which is reduced by $M_S(x = 0.01)$ as shown in Fig. 2(b). The calculations of M_s are well in agreement with the experiment data except for the sample with $x = 0.05$, where a large bias between the theoretical calculation and the experimental data may be caused by the crossover of FM ordering from 2D to 3D. The inset of Fig. 2(b) shows the oscillating behavior of the RKKY interaction for $x = 0.02$. This calculation clearly indicates that with increasing Co concentration, the RKKY interaction is enhanced due to the decrease of distances between Co-ion moments. It also indicates that the RKKY interaction be the dominant mechanism for the long-range FM ordering. Comparing with other magnetic impurity doping, such strong RKKY interaction may be originated from the feature of Co, e.g., strong s-d electrons exchange interaction and high Curie temperature. Such strong RKKY interaction has also been observed in other Co-doped compounds.[17] The RKKY interaction needs the charge carriers in the CuO_2 plane, and the charge carriers must also take responsibility for the SC in the superconducting state. How to solve such two roles of charge carriers in the CuO_2 plane? We consider that the existence of two types of charge carriers in electron-doped HTSC[8,9,10] may be important. The previous work[11] has suggested that the two-band model and two kinds of charge carriers in Ru-1212 take responsibility for the existence of SC and FM. Of course, understanding the origin of such coexistence of SC and FM in LCCCO should be probed further.

In order to understand the possible role of charge carriers on SC and FM ordering further, a reduction treatment is carried out for the sample with $x = 0.01$, through

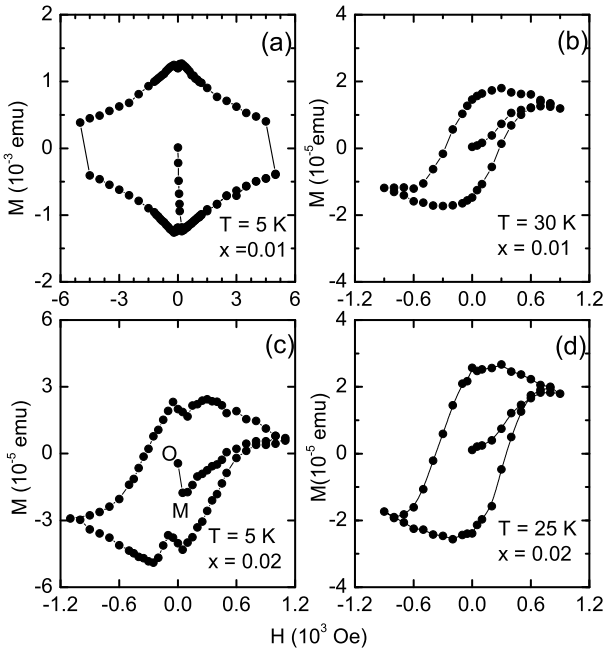

FIG. 3: In-plane Magnetization versus field for LCCCO thin films by zero magnetic field cooling: (a) superconducting magnetization behavior of the film with $x = 0.01$ at 5 K; (b) full FM hysteresis loop of the film with $x = 0.01$ at 30 K; (c) clear evidence for the coexistence of SC and FM of the film with $x = 0.02$ at 5 K, confirmed by the shielding effect in the lower field (indicated by OM, with $H_{c1} \sim 50$ Oe), and the FM hysteresis develops with increasing H; (d) full FM hysteresis loop for the film with $x = 0.02$ at 25 K. All these clearly show the coexistence and competition of SC and FM for the LCCCO films with $x = 0.01$ and 0.02.

which the relative strength of SC and FM will be changed by adjusting the concentrations of charge carriers. The samples with $x = 0.01$ were annealed at $\sim$ 600 K in $\sim$ 10^{-5} Pa vacuum for several minutes. The key for this process is to partially remove the oxygen from the films, but maintain the single T'-phase. After the treatment, XRD data show that the films are still single T'-phase. Fig. 4(a) shows the evolution of the M_S with the annealing times. It shows that at 15 K the M_S is about 2.8 times larger after the first time annealing in vacuum, and then keeps almost constant for the further annealing steps, whereas T_{c0} decreases from 13 K before reduction treatment (the case of as-apical-oxygen removing) to $<$ 5 K after the third time annealing.

In order to reveal the origin of the changes of SC and FM with the reduction treatment, the X-ray Photoelectron Spectroscopy (XPS) measurements were performed with an AXIS-Ultra instrument from Kratos. The valences of La, Ce, Co and Cu were tested before and after the reduction treatment. The results clearly show that after reduction treatment, the main peak of the Cu $2p_{3/2}$ state changes from 934.3 eV to 932.5 eV, and the ratio of the Cu $2p_{3/2}$ satellite peak to Cu $2p_{3/2}$ main peak de-

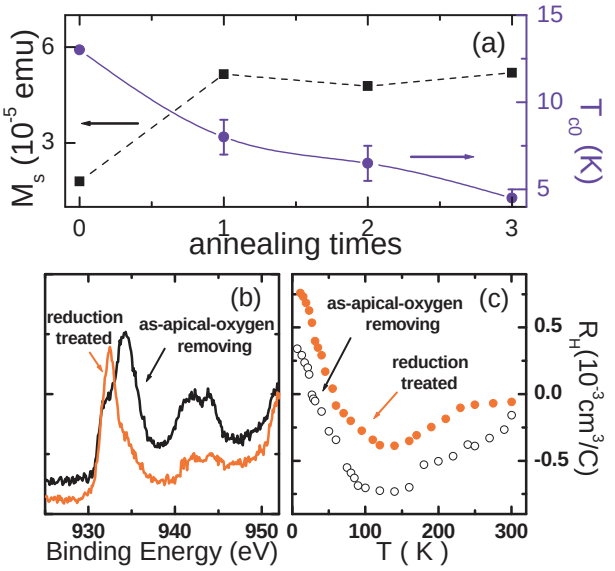

FIG. 4: (color online) (a) M_S (square) and T_{c0} (circle) versus annealing times, the reduction treatment enhances FM to high level, whereas T_{c0} is decreased remarkably, which is caused by the reduction of the valence of Cu. (b) and (c) Cu $2p_{3/2}$ core-level XPS spectra and Hall coefficient of the cases of as-apical-oxygen removing and reduction-treated LCCCO with $x = 0.01$, respectively.

creases as shown in Fig. 4(b). That is, the valence of partial Cu ions changes from +2 to +1.[22] While the valences of La, Ce and Co have no detectable changes. The valence change of Cu presents that the reduction process preferentially removes the oxygen O(1) from the CuO_2 plane, rather than the O(2) in La-O plane, which is similar to that induced by the reduction process in NCCO ,[23] where the oxygen was removed first from the CuO_2 plane with the reduction treatment. Owing to the reduction of Cu ions, this process should result in the decrease of the concentration of the electrons in the CuO_2 plane and weakens the SC. However, the RKKY interaction is enhanced (M_S increases) after reduction treatment, so the concentration of holes possibly increases (the RKKY interaction needs the charge carriers). From the Hall measurements as shown in Fig. 4(c), we find that the Hall coefficient is shifted towards positive direction after reduction treatment indeed. Therefore, the decrease of T_c should be attributed to the reduction of the concentration of electrons. This means that the electrons may play an important role for SC in the LCCO, which seems to be different from the point of view that the holes are more important to SC in the NCCO.[24]

In conclusion, the optimally doped LCCO thin films are investigated by dilute magnetic impurity Co doping at the Cu site. It is observed for the first time that the long-range FM ordering appears at the temperature range from 5 K to 300 K for all the LCCCO thin films, $x = 0.01 - 0.05$, which is suggested to be formed by the RKKY interaction; the coexistence of SC and FM is observed in the very dilute Co concentrations, $x = 0.01$ and 0.02, below T_c. The existence of two kinds of charge carriers in the electron-doped HTSC is suggested to be an important reason to such coexistence. However, other reason, such as that the Co-ion may have some special feature when it is doped in electron-doped HTSC, should also be considered. Based on the reduction experiment, we argue that the electrons play an important role for SC in LCCO system. We believe that the present work provides new information for understanding the intrinsic feature of the electron-doped HTSC.

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* Electronic address: brzhao@aphy.iphy.ac.cn

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